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Comparative study on open system digestion vs. microwave-assisted digestion methods for trace element analysis in agricultural soils

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Abstract

The aim of this work was to evaluate two different digestion procedures for the determination of the concentration of trace and major elements (As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sb, V, Zn) in five hundred randomly selected soil samples from LUCAS Soil Survey. The two procedures employed in sample preparation are the open vessel digestion, which is described in the ISO 11466:1995 [1], and the microwave assisted digestion, implemented in the prEN16174 document [2].

Certified Reference Materials (NIST 2711 and BCR 141R) were also analysed using both pre-treatment approaches in order to determine sample recoveries and assess quality assurance and quality control (QA/QC) of the methods.

Results obtained with samples and CRMs analysis are useful to compare the two tested digestion procedures for recovery rate, safety, cost and time taken.

The results obtained from reference materials and soil samples revealed a good agreement between both procedures and the certified values. T-test was also employed to evaluate the hypothesis of equal mean between concentration determined after the open vessel and microwave-assisted digestions. This test demonstrates that, for the majority of the elements, the hypothesis is verified. The microwave procedure was then recommended as the method for the digestion of the 22 000 soil samples of the LUCAS Soil Survey, based on good precision and accuracy, speed and safety.

Keywords: Microwave assisted digestion - Open system digestion - Soil samples

List of Abbreviations and Symbols

Throughout this report the following abbreviations and symbols are used:

BCR	Community Bureau of Reference
CEN	European Committee for Standardization
CRM	Certified Reference Material
ESDAC	European Soil Data Centre
EU	European Union
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
ISO	International Organization for Standardization
IUPAC	International Union for Pure and Applied Chemistry
JRC	Joint Research Centre
LIMS	Laboratory Information Management System
LUCAS	Land Use/Cover Area frame Statistical Survey
NIST	National Institute of Standards and Technology
MW	Microwave
OV	Open Vessel
QA/QC	Quality Assurance/Quality Control
SDV	Standard Deviation
SRM	Standard Reference Material

Note that chemical elements are identified and expressed according to IUPAC rules.

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1. Introduction

The LUCAS Programme - the periodic Land Use/Land Cover Area Frame Survey – organised and managed by Eurostat (the statistical office of the European Union) started in 2001. The survey is based on the visual assessment of land parameters that are deemed relevant for agricultural policy. Since 2006 the sampling design is based on the intersection of a regular 2 km x 2 km grid covering the territory of the EU. This results in around 1,000,000 geo-referenced points (Eurostat 2010).

In 2009 the European Commission has extended the LUCAS from visual land cover assessment to sampling and analysis of the main properties of topsoil across the Union. This topsoil survey - although limited to the upper layer of soil cover (usually regarded as the uppermost 20-30 cm) - represents the first effort to build a consistent spatial database of the soil cover across the EU based on standard sampling and analytical procedures, with the analysis of all soil samples being carried out in a single laboratory. In addition, the LUCAS Topsoil Survey has the potential to be the basis for an EU wide harmonised soil monitoring. As a result, approximately 22.000 soil samples were collected and submitted for analysis.

The first set of soil analysis targeted basic soil physical and chemical attributes, which are considered to be most relevant for agricultural and environmental indicators [1]. Next, the Inorganic Chemistry Laboratory of the Joint research Centre was commissioned to analyse the soil samples for trace elements. The studied elements include As, Cd, Co, Cr, Cu, Fe, Hg, Ni, Mg, Mn, P, Pb and V, Zn. The JRC laboratory performing this study is certified according to ISO 9001 and operates all its procedures in full alignment with the general requirements of the organization’s quality policy. All procedures are carefully documented and results of measurements are managed using a LIMS (Laboratory Information Management System), which fulfils the requirements of ISO 9001/ISO 17025.

This work was completed in early 2014 and the result of the analyses will be integrated to the database of the European Soil Data Centre (ESDAC). The data set is of particular relevance to establish a baseline for diffuse pollution across the EU.

The current study was preceded by a study on trace elements published by the JRC in 2006, which addressed the issue of establishing background values in European soils. The study of 2006 presented the results for the elements Cd, Cr, Cu, Hg, Ni, Pb, and Zn after harmonization to *aqua regia* basis by using conversion algorithms. Parallel to this study, a large-scale standardization project was mandated by the Commission to CEN (Mandate M 320), with the task to produce across-matrix applicable measurement standards for soil, sludge and bio-waste analyses.

As the standard digestion method using aqua regia as extracting agent is rather costly, time consuming and also presents a higher safety risk due to the strong reagent, development of a rapid, safer and cheaper method was considered to be necessary.

Therefore we applied an alternative digestion method - using microwave - on the same samples to assess the effect the pretreatment on the final accuracy and reliability of the results.

The work presented in this report evaluated the equivalence between microwave-assisted digestion and open-vessel digestion. Both techniques were evaluated in a comparison on a subset of soils (500 samples). The findings of this comparison are published in the present technical report.

The quantified accuracy measure of the employed alternative digestion method shows that it could be a reasonable substitute for the aqua regia based pre-treatment for detecting trace elements in soil on a long term. Thus, monitoring these elements in European soils can be performed safer in a more cost-effective manner.

2. Experimental methods

2.1 Reagents

Deionized water with a resistivity of 18.2 MΩ cm, produced by a Milli-Q Plus pure water generating system from MILLIPORE Gradient A10, was used for standards and sample solutions preparation.

Trace analytical-grade 65% nitric acid (NO_3, suprapur® - Merck) and 37% hydrochloric acid (HCl, suprapur® - Merck) were used for sample digestion.

Calibration solutions for ICP-OES were prepared by stepwise dilution: the calibration standard solutions were prepared by diluting single element stock standard solutions with single or double-Milli-Q water step by step to make the concentration of interest.

2.2 Sample preparation

Prior to analytical determination, soil samples were air-dried in order to remove all water content. Obtained dried samples were grounded in an agate ball mixer up to a particle size of 630 µm in order to provide a homogenized powder.

Certified reference materials (CRMs) were furnished in homogeneous and dried powders at a size lower than 90 µm and no pre-treatment was necessary.

Trace and major elements analysis by ICP-OES technique also requires digested samples: digestion was made with both microwave-assisted and open vessel digestion.

2.3 Microwave-assisted digestion

A Multiwave 3000 microwave device (Anton Paar) was employed for sample digestion. The followed procedure is descibed in the prEN16174 document [2]. About 0.1g of soil sample was weighed in a microwave vessel using an electronic balance (Mettler AT261, Mettler Instruments Corp) with a precision of 1 µg. The mixture of *aqua regia*, i.e. 1.5 mL of HNO_3 and 4.5 mL HCl, was carefully added to each test portion and the vessel was gently shaken, sealed and placed in the microwave oven under previously optimized operating conditions [3]. Aqua regia mixture was used as blank solution.

The microwave autoclave can digest up to 48 samples in the reaction chamber simultaneously under identical experimental conditions. The maximum pressure of the reaction chamber with sample vessels inside was set to 1225 bar. Then, the vessels were heated in the microwave autoclave for 35 min reaching a temperature of maximum 140 °C and a pressure of approximately 20 bar. Before opening the reaction chamber, the digests were allowed to cool for about 180 min to well below the boiling point of the acid mixture at atmospheric pressure.

Each extract was filtered in a 50 mL glass flask using a vacuum pump system and a Millipore Millex® HN Nylon syringe Driven Filters with 0.45µm pore size. The vessel and the vessel cup were subsequently rinsed three times with Milli-Q water and the rinse water was filtered in the same flask. At the end, the flask was made up to volume. The experimental apparatus is shown in Figure 1. Digests were stored at 4 ºC until analyses by inductively coupled plasma-optical emission spectrometry.

2.4 Open vessel digestion

The aqua regia extraction was based on the procedure recommended by the International Organization for Standardization (ISO) [4].

The samples were weighted in Teflon beakers with a pre-determined amount of acid mixture (9 ml of 37% hydrochloric acid and 3 ml of 65% nitric acid). Approximately 0.2 g of soil sample was used.

The pre-digestion step was done at room temperature for 16 h followed by boiling under reflux at 145 ºC for 2 h. The obtained suspension was filtered through an ashless Whatman 542 filter and then diluted to 100 ml with Milli-Q water. Extracted samples were stored in polyethylene bottles until analyses by inductively coupled plasma-optical emission spectrometry.

The apparatus for open vessel digestion is illustrated in Figure 2.

Figure 1 - Micro-wave assisted digestion device

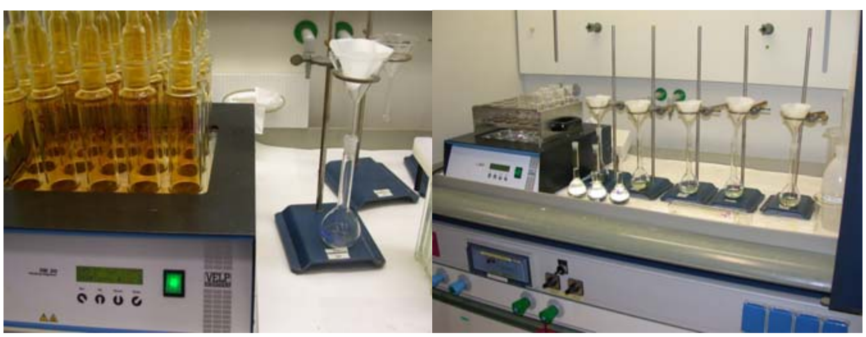


Figure 2 - Extraction of trace elements using aqua regia methods in accordance with ISO 11466

2.5 Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES)

The concentrations of elements (As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sb, V, Zn) in digests were measured by optical emission spectrometry with inductively coupled argon plasma as the excitation source. The method was previously validated according to the ISO 17025 requirements [3] and the adopted operating procedure for sample analysis is based on the prEN16170 document [5].

The method describes the multi-elemental determination of elements in aqueous solutions and digests by simultaneous optical ICP-OES with axial or radial viewing of the plasma. The Optima 2100 DV ICP-OES device by Perkin Elmer was employed for this study (Figure 3). The operating conditions used for digests are listed in Table 1.

Table 1 - Operating conditions for the Optima 2100 DV ICP-OES

Instrument part	Parameter	Value
Plasma condition	Plasma flow (Argon)	15 L/min
	Auxiliary flow (Argon)	0.2 L/min
	Nebulizer flow (Argon)	0.8 L/min
	Power	1300 W
	View distance	15
	Plasma view	axial
Peristaltic pump	Sample flow rate	1.5 L/min
Autosampler	Wash between samples	30s

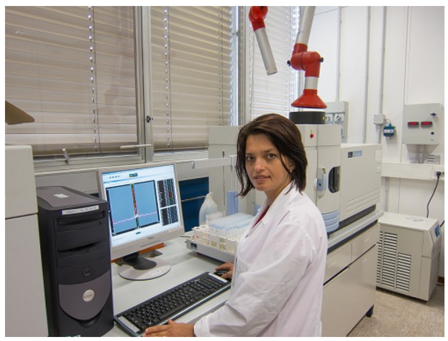


Figure 3 - Optima 2100 DV ICP-OES device operated at the JRC

3. Results and discussion

Microwave-assisted digestion and open vessel digestion approaches were both applied to 500 soil samples and CRMs. A CRM was added to every batch of sample measured in order to assure quality control and quality assurance of the methods. Measured concentrations of trace and major elements by ICP-OES were useful to gain information on the comparability of both sample pre-treatment procedures.

The effectiveness of the applied classical and microwave methods was assessed and discussed.

3.1 Reference materials results

Certificate Reference Materials were analysed together with soil samples, using both digestion approaches. Measured concentrations were compared with certified values to account for method recovery.

Trace and major elements were analysed in BCR 141R ("Calcareous Loam Soil") and NIST 2711 ("Montana Soil") reference materials.

Average recovery for the elements Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn were obtained using the BCR 141R material; recovery results for both MW and OV techniques are listed in Table 2.

Average recovery for the elements As, Cd, Cu, Fe, Mg, Mn, Ni, P, Pb, Sb, V and Zn were measured in NIST 2711 material; recovery results for both MW and OV approaches are listed in Table 3.

Table 2 - Average recovery and standard deviation for BCR 141R (%) obtained with both MW and OV sample pre-treatment

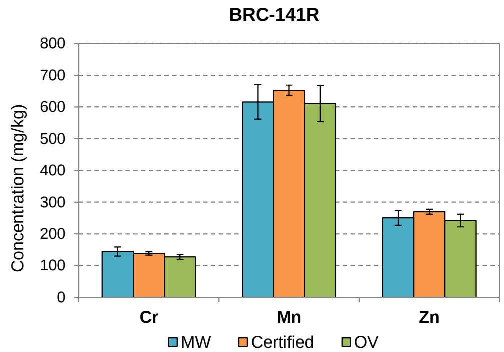
	Microwave assisted (%)		**Open vessel (%)**	
Elements	*Average*	*STD*	*Average*	*STD*
Cd	91.7	8.6	89.7	5.5
Co	108.1	9.1	101.1	7.4
Cr	104.5	10.2	92.4	6.1
Cu	98.2	9.9	96.2	7.3
Mn	94.3	8.3	93.5	8.8
Ni	95.3	10.5	89.9	7.6
Pb	97.6	9.6	98.6	7.9
Zn	92.7	8.5	89.7	7.5

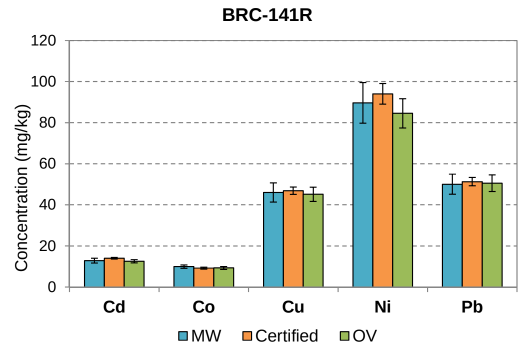
Table 3 - Average recovery and standard deviation for NIST 2711 (%) obtained with both MW and OV sample pre-treatment

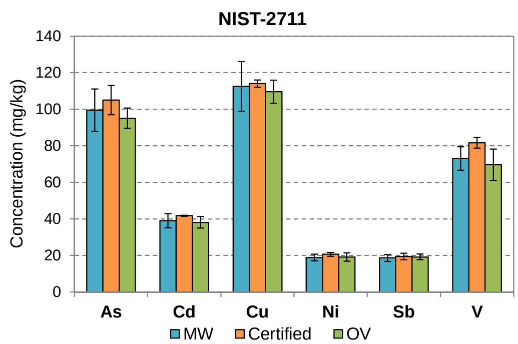
	Microwave assisted (%)		**Open vessel (%)**	
Elements	*Average*	*STD*	*Average*	*STD*
As	94.7	11.1	90.5	5.3
Cd	93.4	9.3	91.3	7.4
Cu	98.7	11.9	96.2	5.5
Fe	92.6	8.9	95.5	5.2
Mg	88.3	7.9	86.6	5.0
Mn	90.0	10.8	89.7	10.8
Ni	91.3	8.8	92.6	11.1
P	97.3	9.0	94.9	9.4
Pb	96.5	8.5	96.6	6.5
Sb	95.9	9.7	98.7	8.0
V	89.4	7.9	85.3	10.5
Zn	90.7	7.8	88.1	5.4

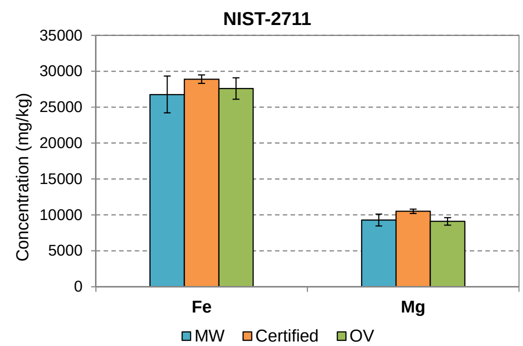
In the BCR 141R standard, average recoveries for the MW procedure were found between 92% and 108%, while for the OV procedure they are in the range 90% - 101%. Average recoveries for NIST 2711 varies from 88% to 99% using the MW approach and from 85% to 99% using the OV procedure. The recovery of each element was computed based on the mean value for BCR 141R and NIST 2711. Certified and measured concentrations, including MW and OV pre-treatment digestions, were also compared in a bar-plot. In

Figure 4, the comparison graphs also include the error bars, which are given by the standard deviation of repeated measurements in the case of measured concentration and by the CRM certificate for certified values.









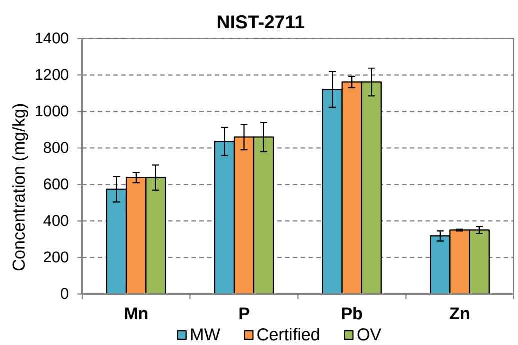


Figure 4 - Certified and measured concentrations in BRC 141R and NIST 2711 for both MW and OV digestion approaches

For BRC 141R, concentrations derived from MW procedure are generally higher than those derived from the open vessel approach. However, except for Cd in the OV, average concentrations with error bars are comparable with certified concentrations.

For NIST 2711, Mg and V for both MW and OV, show concentrations with error bars lower than the certified concentration. In the case of OV approach even the Cd value, including standard deviation, results lower than the certified value. This could be attributed to the use of total certified concentration in NIST 2711 material, instead of the aqua regia content as reported in BCR 141R.

A t-test was used to evaluate the hypothesis of equal mean between concentration derived from the OV and MW pre-treatment approaches. Results of the application of the t-test to element concentration are listed in Table 4 and Table 5. This test demonstrates that, for the majority of the elements, the hypothesis of equal means is verified. For the two elements in the BCR 141R where t-test hypothesis was rejected (Cr and Cu) the hypothesis of higher values for the microwave approach was verified. This could be justified taking into consideration that aqua regia will not totally dissolve most soil and the efficiency of extraction differs from element to element, as well as from matrix type.

Table 4 - t-test results for BCR 141R

Elements	t-test
Cd	true
Co	true
Cr	false
Cu	false
Mn	true
Ni	true
Pb	true
Zn	true

Table 5 - t-test results for NIST 2711

Elements	t-test
As	true
Cd	true
Cu	true
Fe	true
Mg	true
Mn	true
Ni	true
P	true
Pb	true
Sb	true
V	true
Zn	true

3.2 Soil sample results

In order to evaluate the comparison between the microwave-assisted digestion and the open vessel digestion procedure on soil samples, a total of 500 samples extracted from different countries were analysed for trace and major elements by ICP-OES. Fifteen samples were measured from the following countries: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Luxemburg, Malta, Netherland, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden and United Kingdom. Thirteen samples were analysed from Luxemburg and 142 samples were extracted from the Swedish batch.

For a summarising view of all concentration data resulting from the application of both MW and OV technique to 500 samples, a level of acceptance criteria was set to define the comparison degree between the two digestion approaches.

Firstly, two threshold values of 15% and 30% difference between MW and OV concentration values were defined. If MW and OV values of the same soil sample differed by less than 15%, then the comparison level was set to "OK". When the difference in concentration was between 15% and 30% the level was set to "WARNING". In the last case, with a difference in concentration values more than 30%, the comparison was defined as "FAILURE". Finally the "LOD" label was used when both the MW and OV concentrations were below the limit of detection.

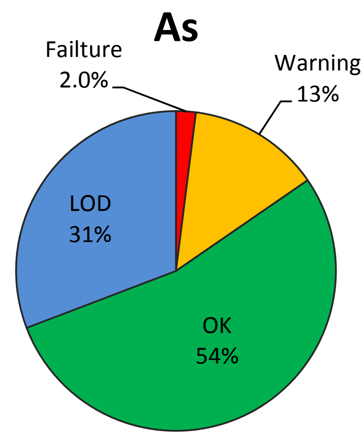
In the particular case where only one concentration value was below the LOD two possibilities arose: if one concentration was below the LOD and the other was below the LOQ, the comparison was set to "LOD" label. On the contrary, if the other concentration was higher than the LOQ, then the acceptance level was computed between the concentration value and the LOQ.

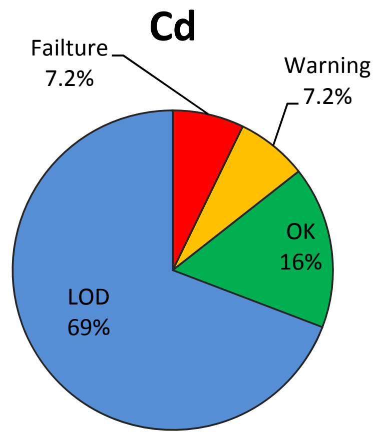
Summary results are express, in percentage terms, in Table 6.

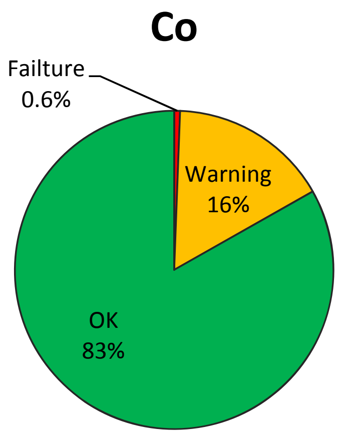
Table 6 - Comparison data between MW and OV, expressed in %

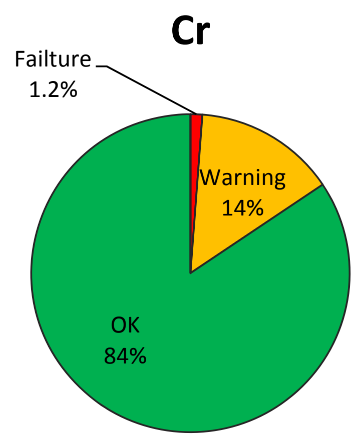
Elements	***OK (%)***	***Warning (%)***	***Failture (%)***	***LoD (%)***
As	53.8	13.4	2.0	30.8
Cd	16.4	7.2	7.2	69.2
Co	83.2	16.2	0.6	0.0
Cr	84.4	14.4	1.2	0.0
Cu	85.4	13.4	1.0	0.2
Fe	89.8	10.2	0.0	0.0
Mg	86.6	13.2	0.2	0.0
Mn	84.8	14.8	0.4	0.0
Ni	85.0	13.6	1.4	0.0
P	92.8	7.2	0.0	0.0
Pb	85.6	13.2	1.0	0.2
Sb	52.8	10.6	8.0	29.0
V	87.2	12.0	0.8	0.0
Zn	88.4	10.4	1.2	0.0

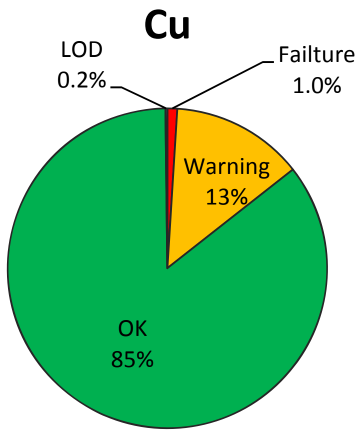
For a better interpretation of numerical results of level of acceptance, pie chart were plotted using the following colour coding: green for "OK", yellow for "WARNING", red for "FAILURE" and blue for "LOD". The pie charts are shown in Figure 5.

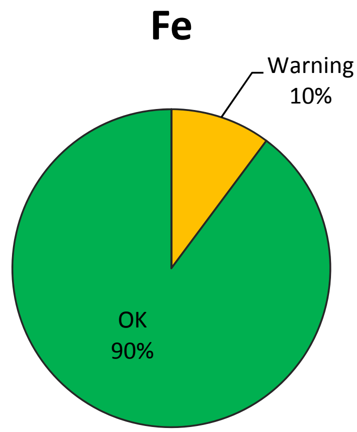

As
Failture 2.0%
Warning 13%
LOD 31%
OK 54%

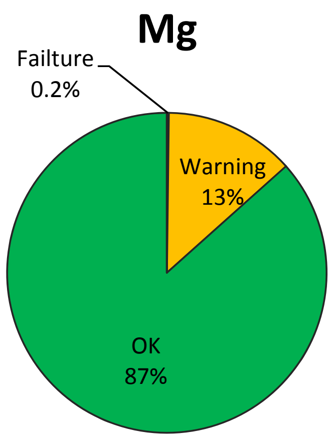

Cd
Failture 7.2%
Warning 7.2%
OK 16%
LOD 69%

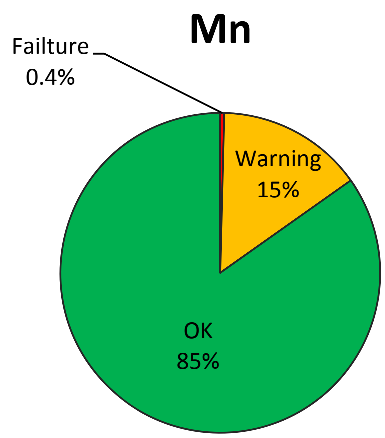

Co
Failture 0.6%
Warning 16%
OK 83%


Cr
Failture 1.2%
Warning 14%
OK 84%


Cu
LOD
0.2%
Failture
1.0%
Warning
13%
OK
85%


Fe
Warning
10%
OK
90%


Mg
Failture
0.2%
Warning
13%
OK
87%


Mn
Failture
0.4%
Warning
15%
OK
85%

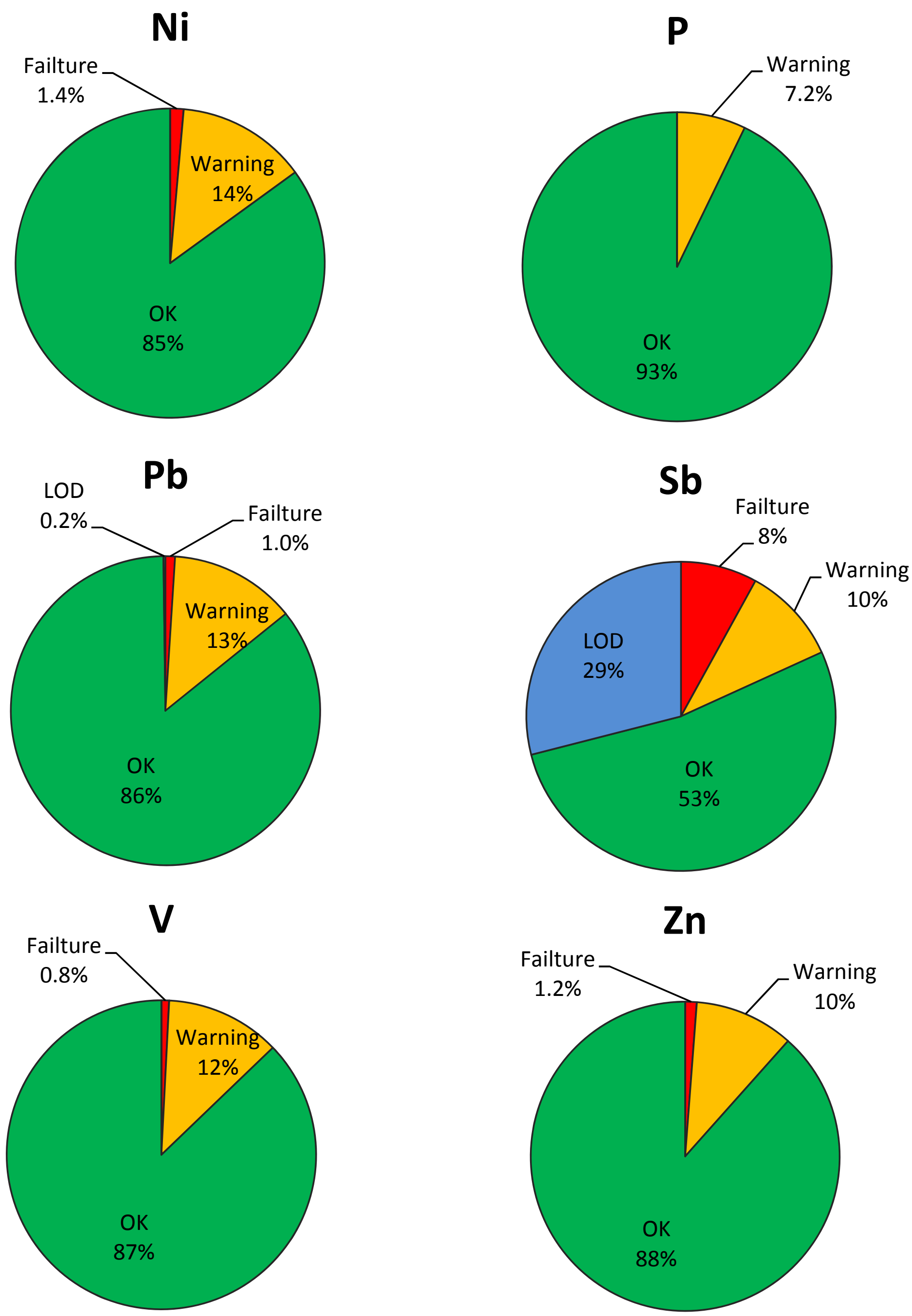


Figure 5 - Pie charts representation of level of acceptance comparison between MW and OV techniques

In Annex A, regression graphs for each analysed element are shown. X-axis represents element concentration obtained after microwave-assisted digestion, while y-axis is the concentration value after open vessel method. A red dot indicates the concentration value measured in the CRM used for QA/QC.

Correlation coefficients, which are also indicated in the graphical representation, range from 0.864 for Cd to 0.988 for Cr.

4. Conclusions

Trace and major elements were investigated in 500 randomly selected soil samples from the Lucas Soil Survey. The final aim was to evaluate the comparison between two sample pre-treatment techniques: the open vessel digestion and the microwave-assisted digestion.

The first method is the conventional ISO approach widely used for its documented procedure, but it is time consuming (up to 18 hours for complete digestion) and requires more reagents and sample quantity.

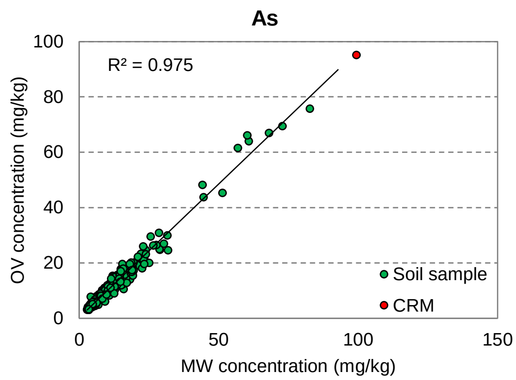
On the contrary, the microwave-assisted approach is only draft-documented, but it takes less than 75 minutes for a complete 48 sample preparation; it is also safer than open vessel because the digestion procedure is applied in a closed system and requires lower reagent and sample usage.

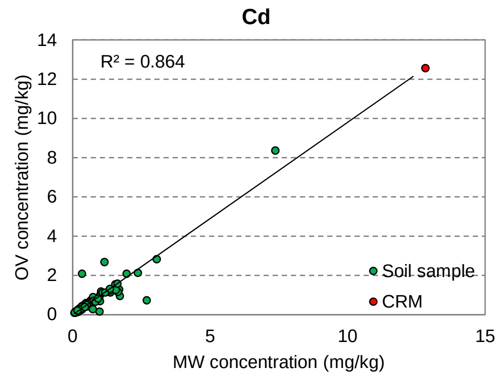
The results obtained from the trace and major element analysis in CRMs provided a good agreement between both techniques. In general, recovery rates are slightly higher for microwave-assisted approach, but the t-test confirm the hypothesis of equal means between concentrations computed on CRMs with both MW and OV pre-treatment. An exception was for Cr and Cu in BCR 141R where MW concentrations were found higher than OV.

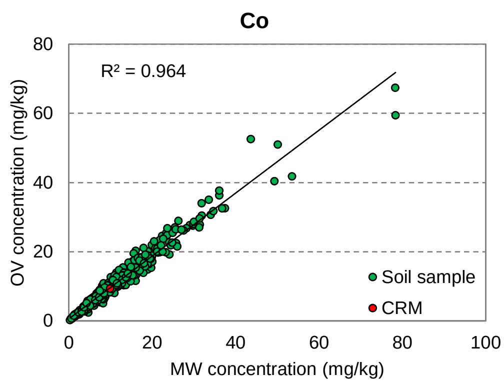
Soil samples analysis confirm the good agreement of both sample preparation techniques, where in the majority of cases, element concentration measured after both pre-treatment approaches differ by less than 15%.

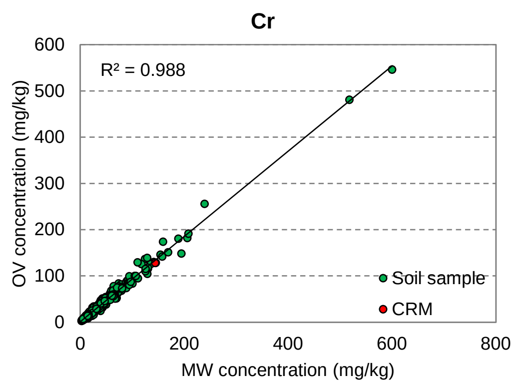
Annex A – Regression curves

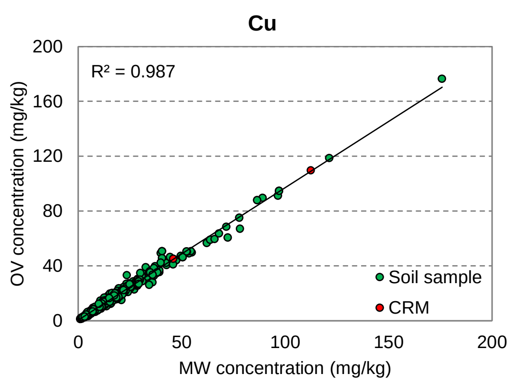
The following graphs represent regression curves between soil samples treated with both microwave assisted digestion (x-axis) and open vessel system (y-axis). A red dot represents the concentration value of CRM used for QA/QC.

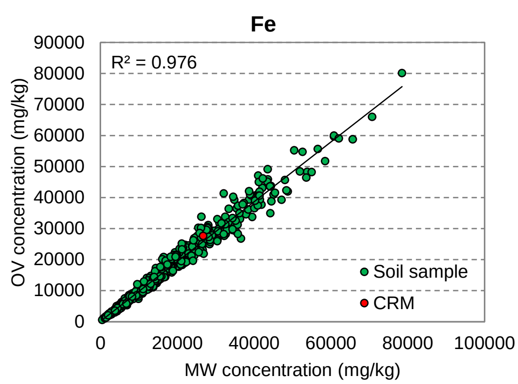


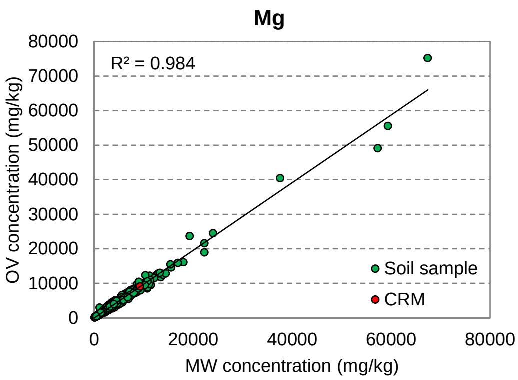


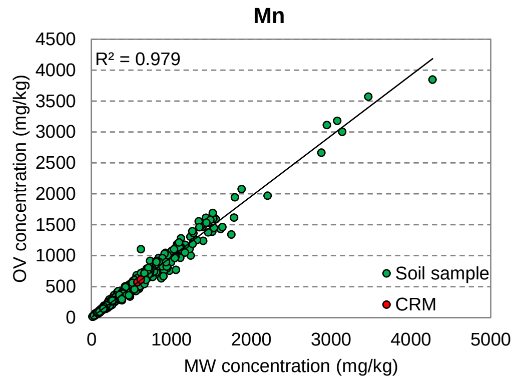


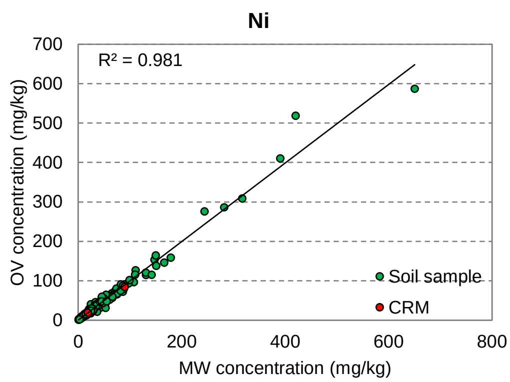


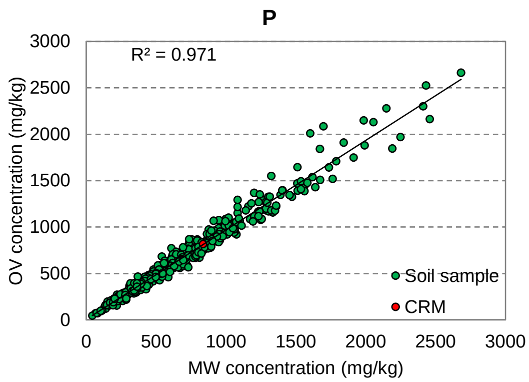


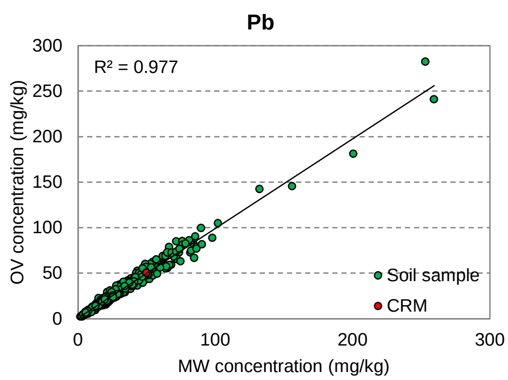


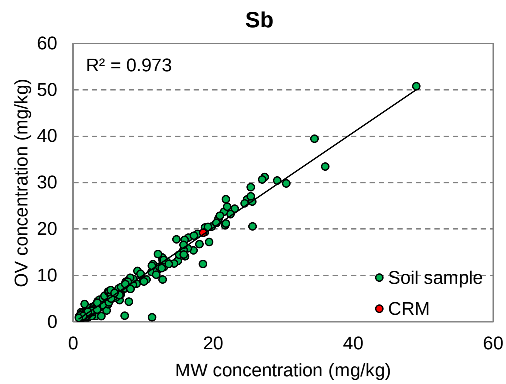

Mg
R² = 0.984
Soil sample
CRM
OV concentration (mg/kg)
MW concentration (mg/kg)

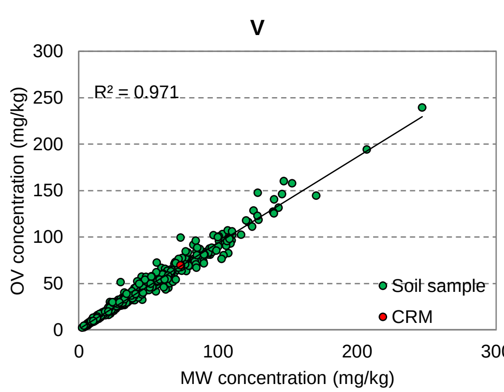

Mn
R² = 0.979
Soil sample
CRM
OV concentration (mg/kg)
MW concentration (mg/kg)

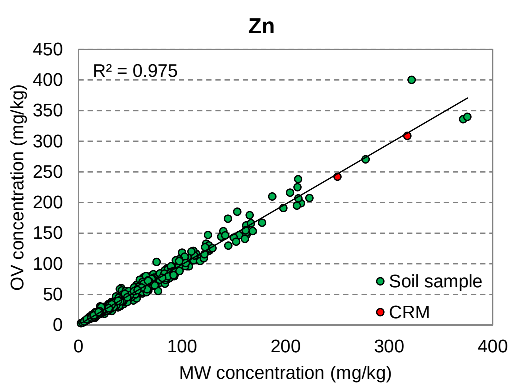

Ni
R² = 0.981
Soil sample
CRM
OV concentration (mg/kg)
MW concentration (mg/kg)


P
R² = 0.971
Soil sample
CRM
OV concentration (mg/kg)
MW concentration (mg/kg)


Pb
R² = 0.977
Soil sample
CRM
OV concentration (mg/kg)
MW concentration (mg/kg)


Sb
R² = 0.973
Soil sample
CRM
OV concentration (mg/kg)
MW concentration (mg/kg)


V
R² = 0.971
Soil sample
CRM
OV concentration (mg/kg)
MW concentration (mg/kg)


Zn
R² = 0.975
Soil sample
CRM
OV concentration (mg/kg)
MW concentration (mg/kg)

Annex B – List of soil samples used in the comparison study

N.	*Country*	*Samples code*	*OV weight(g)*	*MW weight(g)*
1	Estonia	0047_SO_03360_01_00	0.2304	0.1054
2	Estonia	0047_SO_03370_01_00	0.2320	0.1353
3	Estonia	0047_SO_03380_01_00	0.2084	0.1025
4	Estonia	0047_SO_03381_01_00	0.2208	0.1051
5	Estonia	0047_SO_03382_01_00	0.2078	0.1064
6	Estonia	0047_SO_03383_01_00	0.2191	0.1124
7	Estonia	0047_SO_03398_01_00	0.2072	0.1022
8	Estonia	0047_SO_03425_01_00	0.2474	0.1069
9	Estonia	0047_SO_03426_01_00	0.2114	0.1122
10	Estonia	0047_SO_03450_01_00	0.2036	0.1095
11	Estonia	0047_SO_03507_01_00	0.2092	0.1188
12	Estonia	0047_SO_03595_01_00	0.2019	0.1062
13	Estonia	0047_SO_03600_01_00	0.2088	0.1126
14	Estonia	0047_SO_03612_01_00	0.2244	0.1101
15	Estonia	0047_SO_03613_01_00	0.1999	0.1069
16	Finland	0047_SO_06481_01_00	0.2056	0.1027
17	Finland	0047_SO_06624_01_00	0.1973	0.1318
18	Finland	0047_SO_06937_01_00	0.2124	0.1014
19	Finland	0047_SO_07014_01_00	0.2063	0.1006
20	Finland	0047_SO_07031_01_00	0.2148	0.1135
21	Finland	0047_SO_07207_01_00	0.2101	0.1161
22	Finland	0047_SO_07213_01_00	0.2064	0.1179
23	Finland	0047_SO_07279_01_00	0.2021	0.1057
24	Finland	0047_SO_07546_01_00	0.2028	0.1025
25	Finland	0047_SO_07721_01_00	0.2041	0.1022
26	Finland	0047_SO_07750_01_00	0.2069	0.1226
27	Finland	0047_SO_07918_01_00	0.2079	0.1216
28	Finland	0047_SO_07944_01_00	0.2152	0.1268
29	Finland	0047_SO_08318_01_00	0.2038	0.1053
30	Finland	0047_SO_43025_01_00	0.2126	0.113
31	Czech-Republic	0047_SO_0646B_01_00	0.2031	0.1352

32	Czech-Republic	0047_SO_00662_01_00	0.2282	0.1111
33	Czech-Republic	0047_SO_00665_01_00	0.1969	0.1244
34	Czech-Republic	0047_SO_00667_01_00	0.2082	0.1081
35	Czech-Republic	0047_SO_00687_01_00	0.2008	0.1177
36	Czech-Republic	0047_SO_00802_01_00	0.2206	0.1102
37	Czech-Republic	0047_SO_00831_01_00	0.2057	0.1092
38	Czech-Republic	0047_SO_00972_01_00	0.2174	0.1098
39	Czech-Republic	0047_SO_00973_01_00	0.2122	0.1127
40	Czech-Republic	0047_SO_00976_01_00	0.214	0.1062
41	Czech-Republic	0047_SO_01017_01_00	0.2319	0.1098
42	Czech-Republic	0047_SO_01018_01_00	0.2381	0.1092
43	Czech-Republic	0047_SO_01019_01_00	0.2168	0.1068
44	Czech-Republic	0047_SO_01046_01_00	0.2122	0.1056
45	Czech-Republic	0047_SO_01067_01_00	0.2225	0.1109
46	Denmark	0047_SO_03300_01_00	0.2439	0.1142
47	Denmark	0047_SO_03286_01_00	0.2213	0.1255
48	Denmark	0047_SO_03305_01_00	0.2388	0.1364
49	Denmark	0047_SO_03349_01_00	0.2199	0.1208
50	Denmark	0047_SO_03313_01_00	0.2106	0.1155
51	Denmark	0047_SO_03319_01_00	0.1999	0.1179
52	Denmark	0047_SO_03357_01_00	0.2234	0.1416
53	Denmark	0047_SO_03229_01_00	0.2146	0.1321
54	Denmark	0047_SO_03226_01_00	0.2199	0.1063
55	Denmark	0047_SO_03150_01_00	0.2492	0.1211
56	Denmark	0047_SO_03212_01_00	0.2134	0.1241
57	Denmark	0047_SO_03148_01_00	0.1986	0.1122
58	Denmark	0047_SO_03118_01_00	0.2112	0.1047
59	Denmark	0047_SO_03281_01_00	0.2072	0.1058
60	Denmark	0047_SO_03282_01_00	0.2321	0.1188
61	Belgium	0047_SO_00473_01_00	0.2064	0.1199
62	Belgium	0047_SO_0476B_01_00	0.2066	0.1111
63	Belgium	0047_SO_0477B_01_00	0.2312	0.1349
64	Belgium	0047_SO_0487B_01_00	0.2267	0.1123
65	Belgium	0047_SO_0488A_01_00	0.2079	0.1066

66	Belgium	0047_SO_0488B_01_00	0.2112	0.1122
67	Belgium	0047_SO_0492B_01_00	0.2133	0.1065
68	Belgium	0047_SO_0497B_01_00	0.2077	0.1041
69	Belgium	0047_SO_00505_01_00	0.2212	0.1067
70	Belgium	0047_SO_00508_01_00	0.2087	0.1117
71	Belgium	0047_SO_00554_01_00	0.2327	0.1165
72	Belgium	0047_SO_00562_01_00	0.2146	0.1141
73	Belgium	0047_SO_00563_01_00	0.2134	0.1057
74	Belgium	0047_SO_00565_01_00	0.2026	0.1117
75	Belgium	0047_SO_00581_01_00	0.2019	0.1032
76	Austria	0047_SO_00001_01_00	0.2167	0.1074
77	Austria	0047_SO_00002_01_00	0.2029	0.1014
78	Austria	0047_SO_00004_01_00	0.2077	0.1011
79	Austria	0047_SO_00015_01_00	0.2022	0.1058
80	Austria	0047_SO_00017_01_00	0.2222	0.1407
81	Austria	0047_SO_00019_01_00	0.2006	0.1036
82	Austria	0047_SO_00040_01_00	0.2151	0.1143
83	Austria	0047_SO_00047_01_00	0.2085	0.1144
84	Austria	0047_SO_00151_01_00	0.2024	0.1298
85	Austria	0047_SO_00160_01_00	0.2117	0.1193
86	Austria	0047_SO_00161_01_00	0.2235	0.1168
87	Austria	0047_SO_00167_01_00	0.2043	0.0996
88	Austria	0047_SO_00221_01_00	0.2157	0.1176
89	Austria	0047_SO_00372_01_00	0.2121	0.1224
90	Austria	0047_SO_00464_01_00	0.2056	0.1097
91	Ireland	0047_SO_12773_01_00	0.2032	0.1026
92	Ireland	0047_SO_12774_01_00	0.2222	0.1326
93	Ireland	0047_SO_12775_01_00	0.2085	0.1012
94	Ireland	0047_SO_12776_01_00	0.2222	0.1095
95	Ireland	0047_SO_12832_01_00	0.2221	0.1097
96	Ireland	0047_SO_12834_01_00	0.2027	0.1257
97	Ireland	0047_SO_12892_01_00	0.2058	0.1046
98	Ireland	0047_SO_12893_01_00	0.2178	0.1248
99	Ireland	0047_SO_12894_01_00	0.2125	0.1052

100	Ireland	0047_SO_12895_01_00	0.2188	0.1041
101	Ireland	0047_SO_12901_01_00	0.2111	0.1072
102	Ireland	0047_SO_12903_01_00	0.2228	0.1022
103	Ireland	0047_SO_12946_01_00	0.2212	0.1208
104	Ireland	0047_SO_12950_01_00	0.2134	0.1138
105	Ireland	0047_SO_12951_01_00	0.2111	0.1132
106	France	0047_SO_08493_01_00	0.2204	0.1135
107	France	0047_SO_08525_01_00	0.2165	0.1341
108	France	0047_SO_08913_01_00	0.2068	0.1251
109	France	0047_SO_08966_01_00	0.2139	0.1287
110	France	0047_SO_09127_01_00	0.2295	0.1316
111	France	0047_SO_09309_01_00	0.2081	0.1155
112	France	0047_SO_09519_01_00	0.2168	0.1157
113	France	0047_SO_09649_01_00	0.2111	0.1225
114	France	0047_SO_10069_01_00	0.2005	0.1267
115	France	0047_SO_10220_01_00	0.2013	0.107
116	France	0047_SO_10519_01_00	0.2142	0.1334
117	France	0047_SO_10968_01_00	0.1996	0.108
118	France	0047_SO_10992_01_00	0.2187	0.1079
119	France	0047_SO_10995_01_00	0.2109	0.1027
120	France	0047_SO_10998_01_00	o.2123	0.1019
121	Latvia	0047_SO_15245_01_00	0.2011	0.1373
122	Latvia	0047_SO_15255_01_00	0.2003	0.1175
123	Latvia	0047_SO_15257_01_00	0.2095	0.1094
124	Latvia	0047_SO_15272_01_00	0.2184	0.1222
125	Latvia	0047_SO_15334_01_00	0.2141	0.1073
126	Latvia	0047_SO_15369_01_00	0.2266	0.1103
127	Latvia	0047_SO_15386_01_00	0.2094	0.1125
128	Latvia	0047_SO_15458_01_00	0.2088	0.1298
129	Latvia	0047_SO_15463_01_00	0.2341	0.1214
130	Latvia	0047_SO_15487_01_00	0.2294	0.11
131	Latvia	0047_SO_15497_01_00	0.2076	0.1268
132	Latvia	0047_SO_15499_01_00	0.2277	0.1142
133	Latvia	0047_SO_15501_01_00	0.2301	0.1097

134	Latvia	0047_SO_15502_01_00	0.2128	0.1182
135	Latvia	0047_SO_15503_01_00	0.2127	0.1092
136	Hungary	0047_SO_12232_01_00	0.2046	0.1145
137	Hungary	0047_SO_12249_01_00	0.2267	0.1115
138	Hungary	0047_SO_12260_01_00	0.1997	0.1134
139	Hungary	0047_SO_12332_01_00	0.2014	0.1134
140	Hungary	0047_SO_12343_01_00	0.2197	0.1078
141	Hungary	0047_SO_12350_01_00	0.2013	0.1175
142	Hungary	0047_SO_12441_01_00	0.1974	0.1199
143	Hungary	0047_SO_12444_01_00	0.2315	0.1129
144	Hungary	0047_SO_12474_01_00	0.2097	0.1189
145	Hungary	0047_SO_12497_01_00	0.2019	0.1037
146	Hungary	0047_SO_12502_01_00	0.2156	0.1154
147	Hungary	0047_SO_12504_01_00	0.2225	0.1134
148	Hungary	0047_SO_12654_01_00	0.2132	0.1065
149	Hungary	0047_SO_12711_01_00	0.2212	0.1172
150	Hungary	0047_SO_12716_01_00	0.2032	0.1135
151	Portugal	0047_SO_17635_01_00	0.2009	0.1042
152	Portugal	0047_SO_17650_01_00	0.2322	0.1234
153	Portugal	0047_SO_17762_01_00	0.2003	0.1238
154	Portugal	0047_SO_17769_01_00	0.2093	0.1113
155	Portugal	0047_SO_17795_01_00	0.205	0.1174
156	Portugal	0047_SO_17923_01_00	0.2145	0.1178
157	Portugal	0047_SO_17937_01_00	0.2146	0.1253
158	Portugal	0047_SO_17957_01_00	0.2149	0.1266
159	Portugal	0047_SO_18019_01_00	0.2275	0.1286
160	Portugal	0047_SO_18022_01_00	0.2122	0.1098
161	Portugal	0047_SO_18047_01_00	0.2117	0.1477
162	Portugal	0047_SO_18087_01_00	0.2031	0.1298
163	Portugal	0047_SO_18102_01_00	0.2159	0.1189
164	Portugal	0047_SO_18109_01_00	0.2192	0.1125
165	Portugal	0047_SO_18111_01_00	0.2063	0.1168
166	Slovakia	0047_SO_20936_01_00	0.2061	0.1328
167	Slovakia	0047_SO_20937_01_00	0.2055	0.1279

168	Slovakia	0047_SO_20938_01_00	0.2161	0.1189
169	Slovakia	0047_SO_20939_01_00	0.2173	0.1152
170	Slovakia	0047_SO_20940_01_00	0.2041	0.1421
171	Slovakia	0047_SO_20941_01_00	0.2028	0.1349
172	Slovakia	0047_SO_20942_01_00	0.2294	0.1357
173	Slovakia	0047_SO_20943_01_00	0.2038	0.1038
174	Slovakia	0047_SO_20944_01_00	0.2118	0.1133
175	Slovakia	0047_SO_20948_01_00	0.2092	0.1386
176	Slovakia	0047_SO_20951_01_00	0.2136	0.1291
177	Slovakia	0047_SO_20953_01_00	0.2095	0.1331
178	Slovakia	0047_SO_20963_01_00	0.2087	0.1239
179	Slovakia	0047_SO_21072_01_00	0.2088	0.1166
180	Slovakia	0047_SO_21073_01_00	0.2187	0.1064
181	Italy	0047_SO_13241_01_00	0.2228	0.1134
182	Italy	0047_SO_13245_01_00	0.2248	0.1228
183	Italy	0047_SO_13252_01_00	0.2156	0.1194
184	Italy	0047_SO_13256_01_00	0.2247	0.1092
185	Italy	0047_SO_13313_01_00	0.2301	0.1016
186	Italy	0047_SO_13354_01_00	0.2308	0.1397
187	Italy	0047_SO_13355_01_00	0.2173	0.1102
188	Italy	0047_SO_14148_01_00	0.2353	0.1077
189	Italy	0047_SO_14370_01_00	0.2091	0.1183
190	Italy	0047_SO_14371_01_00	0.2153	0.1088
191	Italy	0047_SO_14372_01_00	0.2013	0.1062
192	Italy	0047_SO_14390_01_00	0.2081	0.1438
193	Italy	0047_SO_14413_01_00	0.2153	0.1199
194	Italy	0047_SO_14565_01_00	0.2222	0.1245
195	Italy	0047_SO_14577_01_00	0.2111	0.1075
196	Germany	0047_SO_01269_01_00	0.2056	0.1247
197	Germany	0047_SO_01326_01_00	0.2257	0.1022
198	Germany	0047_SO_01339_01_00	0.2305	0.1055
199	Germany	0047_SO_01392_01_00	0.2217	0.1033
200	Germany	0047_SO_01640_01_00	0.2171	0.1287
201	Germany	0047_SO_01697_01_00	0.2352	0.0952

202	Germany	0047_SO_01707_01_00	0.2095	0.1121
203	Germany	0047_SO_02278_01_00	0.2159	0.1137
204	Germany	0047_SO_02288_01_00	0.2089	0.1291
205	Germany	0047_SO_02429_01_00	0.2198	0.1009
206	Germany	0047_SO_02456_01_00	0.2098	0.1151
207	Germany	0047_SO_02457_01_00	0.2076	0.1068
208	Germany	0047_SO_02597_01_00	0.2255	0.1116
209	Germany	0047_SO_02665_01_00	0.2352	0.1197
210	Germany	0047_SO_02869_01_00	0.2035	0.1036
211	Poland	0047_SO_16160_01_00	0.2031	0.1112
212	Poland	0047_SO_16399_01_00	0.2226	0.1308
213	Poland	0047_SO_16409_01_00	0.2323	0.1222
214	Poland	0047_SO_16504_01_00	0.2078	0.142
215	Poland	0047_SO_16659_01_00	0.2113	0.1765
216	Poland	0047_SO_16677_01_00	0.2043	0.0997
217	Poland	0047_SO_16697_01_00	0.2228	0.1099
218	Poland	0047_SO_16732_01_00	0.2198	0.1045
219	Poland	0047_SO_16733_01_00	0.2229	0.1277
220	Poland	0047_SO_16744_01_00	0.2042	0.1159
221	Poland	0047_SO_17245_01_00	0.2085	0.1159
222	Poland	0047_SO_17251_01_00	0.2021	0.1094
223	Poland	0047_SO_17426_01_00	0.2145	0.1055
224	Poland	0047_SO_17511_01_00	0.2026	0.1118
225	Poland	0047_SO_17532_01_00	0.2296	0.1442
226	Netherland	0047_SO_15609_01_00	0.2056	0.1154
227	Netherland	0047_SO_15611_01_00	0.2053	0.1128
228	Netherland	0047_SO_15612_01_00	0.2297	0.1217
229	Netherland	0047_SO_15623_01_00	0.2226	0.1388
230	Netherland	0047_SO_15711_01_00	0.2133	0.1094
231	Netherland	0047_SO_15714_01_00	0.2084	0.1145
232	Netherland	0047_SO_15740_01_00	0.2302	0.1143
233	Netherland	0047_SO_15741_01_00	0.2292	0.1009
234	Netherland	0047_SO_15743_01_00	0.2192	0.1064
235	Netherland	0047_SO_15744_01_00	0.2154	0.1047

236	Netherland	0047_SO_15745_01_00	0.2123	0.1075
237	Netherland	0047_SO_15804_01_00	0.2174	0.1075
238	Netherland	0047_SO_15811_01_00	0.2226	0.1109
239	Netherland	0047_SO_15814_01_00	0.2335	0.1113
240	Netherland	0047_SO_15819_01_00	0.2025	0.1181
241	UK	0047_SO_21081_01_00	0.2052	0.1122
242	UK	0047_SO_21095_01_00	0.1989	0.1061
243	UK	0047_SO_21096_01_00	0.2073	0.1024
244	UK	0047_SO_21241_01_00	0.2302	0.1065
245	UK	0047_SO_21386_01_00	0.2391	0.1053
246	UK	0047_SO_21405_01_00	0.224	0.1163
247	UK	0047_SO_21462_01_00	0.2201	0.1182
248	UK	0047_SO_21835_01_00	0.228	0.124
249	UK	0047_SO_21937_01_00	0.2006	0.1135
250	UK	0047_SO_21939_01_00	0.2176	0.1237
251	UK	0047_SO_22309_01_00	0.2205	0.1142
252	UK	0047_SO_22319_01_00	0.2279	0.1045
253	UK	0047_SO_22335_01_00	0.2325	0.1213
254	UK	0047_SO_22336_01_00	0.2176	0.1045
255	UK	0047_SO_22433_01_00	0.2147	0.1205
256	Greece	0047_SO_11547_01_00	0.2116	0.1155
257	Greece	0047_SO_11829_01_00	0.2023	0.1179
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500	Sweden	0047_SO_18544_01_00	0.2012	0.1255

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Abstract

The aim of this work was to evaluate two different digestion procedures for the determination of the concentration of trace and major elements (As, Cd, Co, Cu, Cr, Fe, Mg, Mn, Ni, P, Pb, Sb, V, Zn) in five hundred randomly selected soil samples from LUCAS Soil Survey. The two procedures employed in sample preparation are the open vessel digestion, which is described in the ISO 11466:1995 [1], and the microwave assisted digestion, implemented in the prEN16174 document [2].
Certified Reference Materials (NIST 2711 and BCR 141R) were also analysed using both pre-treatment approaches in order to determine sample recoveries and assess quality assurance and quality control (QA/QC) of the methods.
Results obtained with samples and CRMs analysis are useful to compare the two tested digestion procedures for recovery rate, safety, cost and time taken.
The results obtained from reference materials and soil samples revealed a good agreement between both procedures and the certified values. T-test was also employed to evaluate the hypothesis of equal mean between concentration determined after the open vessel and microwave-assisted digestions. This test demonstrates that, for the majority of the elements, the hypothesis is verified. The microwave procedure was then recommended as the method for the digestion of the 22 000 soil samples of the LUCAS Soil Survey, based on good precision and accuracy, speed and safety.

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